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Finite Elements in *Ab Initio* Electronic-Structure Calculations

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Finite Elements in *Ab Initio* Electronic-Structure Calculations

Over the course of the past two decades, the density functional theory (DFT) (see e.g., Jones and Gunnarsson, 1989) of Hohenberg, Kohn, and Sham has proven to be an accurate and reliable basis for the understanding and prediction of a wide range of materials properties from first principles (*ab initio*), with no experimental input or empirical parameters. However, the solution of the Kohn-Sham equations of DFT is a formidable task and this has limited the range of physical systems which can be investigated by such rigorous, quantum mechanical means. In order to extend the interpretive and predictive power of such quantum mechanical theories further into the domain of "real materials", involving nonstoichiometric deviations, defects, grain boundaries, surfaces, interfaces, and the like; robust and efficient methods for the solution of the associated quantum mechanical equations are critical. The finite-element (FE) method (see e.g., Zienkiewicz and Taylor, 1988) is a general method for the solution of partial differential and integral equations which has found wide application in diverse fields ranging from particle physics to civil engineering. Here, we discuss its application to large-scale *ab initio* electronic-structure calculations.

Like the traditional planewave (PW) method (see e.g., Pickett, 1989), the FE method is a variational expansion approach, in which solutions are represented as a linear combination of basis functions. However, whereas the PW method employs a Fourier basis, with every basis function overlapping every other, the FE method employs a basis of strictly local piecewise polynomials, each overlapping only its immediate neighbors. Because the FE basis consists of polynomials, the method is completely general and systematically improvable, like the PW method. Because the basis is strictly local, however, the method offers some significant advantages. First, because the basis functions are localized, they can be concentrated where needed in real space to increase the efficiency of the representation. Second, a variety of boundary conditions can be accommodated, including Dirichlet boundary conditions for molecules or clusters, Bloch boundary conditions for crystals, or a mixture of these for surfaces. Finally, and most significantly for large-scale calculations, the strict locality of the basis facilitates implementation on massively parallel computational architectures by minimizing the need for nonlocal communications. The advantages of such a local, real-space approach in large-scale calculations have been amply demonstrated in the context of finite-difference (FD) methods (see, e.g., Beck, 2000). However, FD methods are not variational expansion methods, and this leads to disadvantages such as limited accuracy in integrations and nonvariational convergence. By retaining the use of a basis while remaining strictly local in real space, FE methods combine significant advantages of both PW and FD approaches.

Finite Element Bases

The construction and key properties of FE bases are perhaps best conveyed in the simplest case: a one-dimensional (1D), piecewise-linear basis. Figure 1 shows the steps involved in the construction of such a basis on a domain $\Omega = (0, 1)$. The domain is partitioned into subdomains called *elements* (Figure 1(a)). In this case, the domain is partitioned into three elements Ω_1–Ω_3; in practice, there are typically many more, so that each element encompasses only a small fraction of the domain. For simplicity, we have chosen a uniform partition, but this need not be the case in general. (Indeed, it is precisely the flexibility to partition the domain as desired which allows for the substantial efficiency of the basis in highly inhomogeneous problems.) A *parent basis* $\hat{\phi}_i$ is then defined on the *parent element* $\hat{\Omega} = (-1, 1)$ (Figure 1(b)). In this case, the parent basis functions are $\hat{\phi}_1(\xi) = (1 - \xi)/2$ and $\hat{\phi}_2(\xi) = (1 + \xi)/2$. Since the parent basis consists of two (independent) linear polynomials, it is complete to linear order, i.e., a linear combination can represent any linear polynomial exactly. Furthermore, it is defined such that each function takes on the value 1 at exactly one point, called its *node*, and vanishes at all (one, in this case) other nodes. *Local basis functions* $\phi_i^{(e)}$ are then generated by transformations $\xi^{(e)}(x)$ of the parent basis functions $\hat{\phi}_i$ from the parent element $\hat{\Omega}$ to each element Ω_e (Figure 1(c)). In present case, for example, $\phi_1^{(1)}(x) \equiv \hat{\phi}_1(\xi^{(1)}(x)) = 1 - 3x$ and $\phi_2^{(1)}(x) \equiv \hat{\phi}_2(\xi^{(1)}(x)) = 3x$, where $\xi^{(1)}(x) = 6x - 1$. Finally, the piecewise-polynomial *basis functions* ϕ_i of the method are generated by piecing together the local basis functions (Figure 1(d)). In the present case, for example,

$$\phi_2(x) = \begin{cases} \phi_2^{(1)}(x), & x \in [0, 1/3] \\ \phi_1^{(2)}(x), & x \in [1/3, 2/3] \\ 0, & \text{otherwise.} \end{cases}$$

The above 1D piecewise-linear FE basis possesses the key properties of all such bases, whether of higher dimension or higher polynomial order. First, the basis functions are strictly local, i.e., nonzero over only a small fraction of the domain. This leads to sparse matrices and scalability, as in FD approaches, while retaining the use of a basis, as in PW approaches. Second, within each element, the basis functions are simple, low-order polynomials, which leads to computational efficiency, generality, and systematic improvability, as in FD and PW approaches. Third, the basis functions are C^0 in nature, i.e., continuous but not necessarily smooth. As we shall discuss, this necessitates extra care in the solution of second-order problems, with periodic boundary conditions in particular. Finally, the basis functions have the key property

$$\phi_i(x_j) = \delta_{ij}$$

i.e., each basis function takes on a value of 1 at its associated node and vanishes at all other nodes. By virtue of this property, an FE expansion $f(x) = \sum_i c_i \phi_i(x)$ has the property $f(x_j) = c_j$, so that the expansion coefficients have a direct, real-space meaning. This eliminates the need for computationally intensive transforms, such as Fourier transforms in PW approaches, and facilitates preconditioning in iterative solutions, such as multigrid in FD approaches (see, e.g., Beck, 2000).

Figure 1(d) shows a general FE basis, capable of representing any piecewise linear function (having the same polynomial subintervals) exactly. To solve a problem subject to vanishing Dirichlet boundary conditions, as occurs in molecular or cluster calculations, one can restrict the basis as in Figure 1(e), i.e., omit boundary functions. To solve a problem subject to periodic boundary conditions, as occurs in solid-state electronic-structure calculations, one can restrict the basis as in Figure 1(f), i.e., piece together local basis functions across the domain boundary in addition to piecing together across interelement boundaries. Regarding this periodic basis, however, it should be noted that an arbitrary linear combination $f(x) = \sum_i c_i \phi_i(x)$ necessarily satisfies

$$f(0) = f(1), \tag{1}$$

but does *not* necessarily satisfy

$$f'(0) = f'(1). \tag{2}$$

Thus, unlike PW or other such smooth bases, while the value condition (1) is enforced by the use of such an FE basis, the derivative condition (2) is not. And so for problems requiring the enforcement of both, as in solid-state electronic-structure, the derivative condition must be enforced by other means (Pask et al., 2001). We address this further in the next section.

Higher-order FE bases are constructed by defining more independent parent basis functions, which requires that some basis functions be of higher order than linear. And, as in the linear case, what is typically done is to define all functions to be of the same order so that, for example, to define a 1D quadratic basis, one would define three quadratic parent basis functions; for a 1D cubic basis, four cubic parent basis functions, etc. With higher-order basis functions, however, come new possibilities. For example, with cubic basis functions there are sufficient degrees of freedom to specify both value and slope at end points, thus allowing for the possibility of both value and slope continuity across interelement boundaries, and so allowing for the possibility of a C^1 (continuous value and slope) rather than C^0 basis. For sufficiently smooth problems, such higher order continuity can yield greater accuracy per degree of freedom and such bases have been used in the electronic-structure context (White et al., 1989; Tsuchida and Tsukada, 1998). However, while straightforward in one dimension, in higher dimensions this requires matching both values and derivatives (including cross terms) across entire curves or surfaces, which becomes increasingly difficult to accomplish and leads to additional constraints on the transformations, and thus meshes, which can be employed (Strang and Fix, 1973).

Higher-dimensional FE bases are constructed along the same lines as the 1D case: partition the domain into elements, define local basis functions within each element via transformations of parent basis functions, and piece together the resulting local basis functions to form the piecewise-polynomial FE basis. In higher dimensions, however, there arises a significant additional choice: that of shape. The most common 2D element shapes are triangles and quadrilaterals. In 3D, tetrahedra, hexahedra (e.g., parallelepipeds), and wedges are among the most common. A variety of shapes have been employed in atomic and molecular calculations (see, e.g., Ram-Mohan, 2002). In solid-state electronic-structure calculations, the domain can be reduced to a parallelepiped, and C^0 (Pask et al., 2001) as well as C^1 (Tsuchida and Tsukada, 1998) parallelepiped elements have been employed.

Solution of the Schrödinger and Poisson Equations

The solution of the Kohn-Sham equations can be accomplished by a number of approaches, including direct minimization of the energy functional (Payne et al., 1992), solution of the associated Lagrangian equations (Arias, 1992), and self-consistent (SC) solution of associated Schrödinger and Poisson equations (see, e.g., Pickett, 1989). A finite-element based energy minimization approach has been described by Tsuchida and Tsukada (Tsuchida and Tsukada, 1998) in the context of molecular and Γ-point crystalline calculations. Here, we shall describe a finite-element based SC approach. In this section, we discuss the solution of the Schrödinger and Poisson equations; in the next, we discuss self-consistency. The solution of such equations subject to Dirichlet boundary conditions, as appropriate for molecular or cluster calculations, is discussed extensively in the standard texts and literature (see, e.g., Zienkiewicz and Taylor, 1988; Ram-Mohan, 2002). Here, we shall discuss their solution subject to boundary conditions appropriate for a periodic (crystalline) solid.

In a perfect crystal, the electronic potential is periodic, i.e.,

$$V(\mathbf{x}+\mathbf{R}) = V(\mathbf{x}) \tag{3}$$

for all lattice vectors $\mathbf{R}$, and the solutions of the Schrödinger equation satisfy Bloch's theorem

$$\psi(\mathbf{x}+\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{x}) \tag{4}$$

for all lattice vectors $\mathbf{R}$ and wavevectors $\mathbf{k}$ (Ashcroft and Mermin, 1976). Thus the values of $V(\mathbf{x})$ and $\psi(\mathbf{x})$ throughout the crystal are completely determined by their values in a single unit cell, and so the solutions of the Poisson and Schrödinger equations in the crystal can be reduced to their solutions in a single unit cell, subject to boundary conditions consistent with Eqs. (3) and (4), respectively.

We consider first the Schrödinger problem:

$$-\tfrac{1}{2}\nabla^2\psi + V\psi = \varepsilon\psi \tag{5}$$

in a unit cell, subject to boundary conditions consistent with Bloch's theorem, where V is an arbitrary periodic potential (atomic units are used throughout, unless otherwise specified).

Since V is periodic, ψ can be written in the form

$$\psi(\mathbf{x}) = u(\mathbf{x})e^{i\mathbf{k}\cdot\mathbf{x}}, \tag{6}$$

where u is a complex, cell-periodic function satisfying $u(\mathbf{x}) = u(\mathbf{x}+\mathbf{R})$ for all lattice vectors $\mathbf{R}$ (Ashcroft and Mermin, 1976). Assuming the form (6), the Schrödinger equation (5) becomes

$$-\tfrac{1}{2}\nabla^2 u - i\mathbf{k}\cdot\nabla u + \tfrac{1}{2}k^2 u + V_L u + e^{-i\mathbf{k}\cdot\mathbf{x}} V_{NL} e^{i\mathbf{k}\cdot\mathbf{x}} u = \varepsilon u, \tag{7}$$

where, allowing for the possibility of nonlocality, V_L and V_{NL} are the local and nonlocal parts of V. From the periodicity condition (4), the required boundary conditions on the unit cell are then (Ashcroft and Mermin, 1976)

$$u(\mathbf{x}) = u(\mathbf{x}+\mathbf{R}_l), \;\; \mathbf{x}\in\Gamma_l \tag{8}$$

and

$$\hat{\mathbf{n}}\cdot\nabla u(\mathbf{x}) = \hat{\mathbf{n}}\cdot\nabla u(\mathbf{x}+\mathbf{R}_l), \;\; \mathbf{x}\in\Gamma_l, \tag{9}$$

where Γ_l and $\mathbf{R}_l$ are the surfaces of the boundary Γ and associated lattice vectors $\mathbf{R}$ shown in Figure 2, and $\hat{\mathbf{n}}$ is the outward unit normal at $\mathbf{x}$. The required Bloch-periodic problem can thus be reduced to the periodic problem (7)–(9).

However, since the domain has been reduced to the unit cell, nonlocal operators require further consideration. In particular, if as is typically the case for *ab initio* pseudopotentials, the domain of definition is all space (i.e., the full crystal), they must be transformed to the relevant finite subdomain (i.e., the unit cell) (Pask and Sterne, 2004). For a separable potential of the usual form

$$V_{NL}(\mathbf{x},\mathbf{x}') = \sum_{n,a,l,m} v^a_{lm}(\mathbf{x}-\boldsymbol{\tau}_a-\mathbf{R}_n) h^a_l v^a_{lm}(\mathbf{x}'-\boldsymbol{\tau}_a-\mathbf{R}_n), \tag{10}$$

where n runs over all lattice vectors and a runs over atoms in the unit cell, the nonlocal term $e^{-i\mathbf{k}\cdot\mathbf{x}} V_{NL} e^{i\mathbf{k}\cdot\mathbf{x}} u$ in Eq. (7) is

$$e^{-i\mathbf{k}\cdot\mathbf{x}} \sum_{n,a,l,m} v^a_{lm}(\mathbf{x}-\boldsymbol{\tau}_a-\mathbf{R}_n) h^a_l \int_{R^3} d\mathbf{x}'\, v^a_{lm}(\mathbf{x}'-\boldsymbol{\tau}_a-\mathbf{R}_n) e^{i\mathbf{k}\cdot\mathbf{x}'} u(\mathbf{x}'),$$

where the integral is over all space. Upon transformation to the unit cell Ω, this becomes

$$e^{-i\mathbf{k}\cdot\mathbf{x}} \sum_{a,l,m}\sum_{n} e^{i\mathbf{k}\cdot\mathbf{R}_n} v^a_{lm}(\mathbf{x}-\boldsymbol{\tau}_a-\mathbf{R}_n) h^a_l \int_{\Omega} d\mathbf{x}' \sum_{n'} e^{-i\mathbf{k}\cdot\mathbf{R}_{n'}} v^a_{lm}(\mathbf{x}'-\boldsymbol{\tau}_a-\mathbf{R}_{n'}) e^{i\mathbf{k}\cdot\mathbf{x}'} u(\mathbf{x}').$$

Having reduced the required problem to a periodic problem on a finite domain, solutions may be obtained using a periodic FE basis. However, if the basis is C^0, as is typically the case, rather than C^1 or smoother, some additional consideration is required. First, the direct application of the Laplacian to such a basis is problematic. Second, being periodic in value but not in derivative (as discussed in the preceding section), the basis does not satisfy the required boundary conditions. Both issues can be resolved by reformulating the original differential formulation in weak (integral) form. Such a weak formulation can be constructed which contains no derivatives higher than first order, and which requires only value-periodicity (i.e., Eq. (8)) of the basis, thus resolving both issues. Such a weak formulation of the required problem (7)–(9) is (Pask et al., 2001): Find scalars ε and functions $u \in \mathcal{V}$ such that

$$\tfrac{1}{2}\int_\Omega d\mathbf{x}\,\nabla v^* \cdot \nabla u + \int_\Omega d\mathbf{x}\, v^*\left(-i\mathbf{k}\cdot\nabla u + \tfrac{1}{2}k^2 u + V_L u + e^{-i\mathbf{k}\cdot\mathbf{x}} V_{NL} e^{i\mathbf{k}\cdot\mathbf{x}} u\right) \\ = \varepsilon \int_\Omega d\mathbf{x}\, v^* u \quad \forall v \in \mathcal{V},$$

where $\mathcal{V} = \{v : v(\mathbf{x}) = v(\mathbf{x}+\mathbf{R}_l),\ \mathbf{x}\in\Gamma_l\}$, and the $\mathbf{x}$ dependence of u and v has been suppressed for compactness.

Having reformulated the problem in weak form, solutions may be obtained using a C^0 FE basis. Letting $u = \sum_j c_j\phi_j$ and $v = \sum_j d_j\phi_j$, where ϕ_j are real periodic finite element basis functions and c_j and d_j are complex coefficients, leads to a generalized Hermitian eigenproblem determining the approximate eigenvalues ε and eigenfunctions u of the weak formulation and thus of the required problem (Pask et al., 2001):

$$\sum_j H_{ij} c_j = \varepsilon \sum_j S_{ij} c_j, \tag{11}$$

where

$$H_{ij} = \int_\Omega d\mathbf{x}\,\left(\tfrac{1}{2}\nabla\phi_i\cdot\nabla\phi_j - i\mathbf{k}\cdot\phi_i\nabla\phi_j + \tfrac{1}{2}k^2\phi_i\phi_j + V_L\phi_i\phi_j + \phi_i e^{-i\mathbf{k}\cdot\mathbf{x}} V_{NL} e^{i\mathbf{k}\cdot\mathbf{x}}\phi_j\right) \tag{12}$$

and

$$S_{ij} = \int_\Omega d\mathbf{x}\,\phi_i\phi_j, \tag{13}$$

and again the $\mathbf{x}$ dependence of ϕ_i and ϕ_j has been suppressed for compactness. For a separable potential of the form (10), the nonlocal term in (12) becomes (Pask and Sterne, 2004)

$$\int_\Omega d\mathbf{x}\,\phi_i(\mathbf{x}) e^{-i\mathbf{k}\cdot\mathbf{x}} V_{NL} e^{i\mathbf{k}\cdot\mathbf{x}} \phi_j(\mathbf{x}) = \sum_{a,l,m} f^{ai}_{lm} h^a_l \left(f^{aj}_{lm}\right)^*,$$

where

$$f^{ai}_{lm} = \int_\Omega d\mathbf{x}\, \phi_i(\mathbf{x}) e^{-i\mathbf{k}\cdot\mathbf{x}} \sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n} v^a_{lm}(\mathbf{x} - \boldsymbol{\tau}_a - \mathbf{R}_n).$$

As in the PW method, the above matrix elements can be evaluated to any desired accuracy, so that the basis need only be large enough to provide a sufficient representation of the required solution, though other functions such as the nonlocal potential may be more rapidly varying. As in the FD method, the above matrices are sparse and structured due to the strict locality of the basis.

Figure 3 shows a series of FE results for a Si pseudopotential (Cohen and Bergstresser, 1966). Since the method allows for the direct treatment of any Bravais lattice, results are shown for a two-atom fcc primitive cell. The figure shows the sequence of band structures obtained for $3 \times 3 \times 3$, $4 \times 4 \times 4$, and $6 \times 6 \times 6$ uniform meshes vs. exact values at selected k points (where "exact values" were obtained from a well converged PW calculation). The variational nature of the method is clearly manifested: the error is strictly positive and the entire band structure converges rapidly and uniformly from above as the number of basis functions is increased. Further analysis (Pask et al., 2001) shows that the convergence of the eigenvalues is in fact sextic, i.e., the error is of order h^6, where h is the mesh spacing, consistent with asymptotic convergence theorems for the cubic-complete case (Strang and Fix, 1973).

The Poisson solution proceeds along the same lines as the Schrödinger solution. In this case, the required problem is

$$-\nabla^2 V_C(\mathbf{x}) = f(\mathbf{x}),\ \ \mathbf{x} \in \Omega \tag{14}$$

subject to boundary conditions

$$V_C(\mathbf{x}) = V_C(\mathbf{x} + \mathbf{R}_l),\ \ \mathbf{x} \in \Gamma_l \tag{15}$$

and

$$\hat{\mathbf{n}} \cdot \nabla V_C(\mathbf{x}) = \hat{\mathbf{n}} \cdot \nabla V_C(\mathbf{x} + \mathbf{R}_l),\ \ \mathbf{x} \in \Gamma_l, \tag{16}$$

where the source term $f(\mathbf{x}) = -4\pi\rho(\mathbf{x})$, $V_C(\mathbf{x})$ is the potential energy of an electron in the charge density $\rho(\mathbf{x})$, and the domain Ω, bounding surfaces Γ_l, and lattice vectors $\mathbf{R}_l$ are again as in Figure 2. Reformulation of (14)–(16) in weak form and subsequent discretization in a real periodic FE basis ϕ_j leads to a symmetric linear system determining the approximate solution $V_C(\mathbf{x}) = \sum_j c_j \phi_j(\mathbf{x})$ of the weak formulation and thus of the required problem (Pask et al., 2001):

$$\sum_j L_{ij} c_j = f_i, \tag{17}$$

where

$$L_{ij} = \int_\Omega d\mathbf{x}\, \nabla\phi_i(\mathbf{x}) \cdot \nabla\phi_j(\mathbf{x}) \tag{18}$$

and

$$f_i = \int_\Omega d\mathbf{x}\, \phi_i(\mathbf{x}) f(\mathbf{x}). \tag{19}$$

As in the FD method, the above matrices are sparse and structured due to the strict locality of the basis, requiring only $O(n)$ storage and $O(n)$ operations for solution by iterative methods, whereas $O(n \log n)$ operations are required in a PW basis, where n is the number of basis functions.

Self-Consistency

The above Schrödinger and Poisson solutions can be employed in a fixed point iteration to obtain the self-consistent solution of the Kohn-Sham equations. In the context of a periodic solid, the process is generally as follows (see, e.g., Pickett, 1989): An initial electronic charge density ρ_e^{in} is constructed (e.g., by overlapping atomic charge densities). An effective potential V_{eff} is constructed based upon ρ_e^{in} (see below). The eigenstates ψ_i of V_{eff} are computed by solving the associated Schrödinger equation subject to Bloch boundary conditions. From these eigenstates, or "orbitals", a new electronic charge density ρ_e is then constructed according to

$$\rho_e = -\sum_i f_i \left|\psi_i\right|^2,$$

where the sum is over occupied orbitals with occupations f_i. If ρ_e is sufficiently close to ρ_e^{in}, then *self-consistency* has been reached; otherwise, a new ρ_e^{in} is constructed based on ρ_e and the process is repeated until self-consistency is achieved. The resulting density minimizes the total energy and is the DFT approximation of the physical density, from which other observables may be derived.

The effective potential can be constructed as the sum of ionic (or nuclear, in an all-electron context), Hartree, and exchange-correlation parts:

$$V_{\mathit{eff}} = V_i^L + V_i^{NL} + V_H + V_{XC}, \tag{20}$$

where, allowing for the possibility of nonlocality, V_i^L and V_i^{NL} are the local and nonlocal parts of the ionic term. For definiteness, we shall assume that the atomic cores are represented by nonlocal pseudopotentials. V_i^{NL} is then determined by the choice of pseudopotential. V_{XC} is a functional of the electronic density determined by the choice of exchange-correlation functional. V_i^L is the Coulomb potential associated with the ions (sum of local ionic pseudopotentials). V_H is the Coulomb potential associated with electrons (the Hartree potential). In the limit of an infinite crystal, V_i^L and V_H are divergent due to the long range $1/r$ nature of the Coulomb interaction, and so their computation requires careful consideration. A common approach is to add and subtract analytic neutralizing densities and associated potentials, solve the resulting neutralized problems, and add analytic corrections (see, e.g., Pickett (1989) in a reciprocal space context, Fattebert and Nardelli (2003) in real space). Alternatively (Pask and Sterne, 2004), it may be noted that the local parts of the ionic potentials $V_{i,a}^L$ associated with each atom can be replaced by corresponding localized ionic charge densities $\rho_{i,a}$ since the potentials fall off as $-Z/r$ (or rapidly approach this behavior) for $r > r_c$, where Z is the number of valence electrons, r is the distance from the ion center, and r_c is on the order of half the nearest neighbor distance. The total Coulomb potential $V_C = V_i^L + V_H$ in the unit cell may then be computed at once by solving the Poisson equation

$$\nabla^2 V_C = 4\pi\rho$$

subject to periodic boundary conditions, where $\rho = \rho_i + \rho_e$ is the sum of electronic and ionic charge densities in the unit cell, and the ionic charge densities $\rho_{i,a}$ associated with each atom a are related to their respective local ionic potentials $V_{i,a}^L$ by Poisson's equation

$$\rho_{i,a} = \nabla^2 V_{i,a}^L / 4\pi.$$

Since the ionic charge densities are localized, their summation in the unit cell is readily accomplished, whereas the summation of ionic potentials is not, due to their long range $1/r$ tails. With V_C determined, V_{eff} can then be constructed as in Eq. (20), and the self-consistent iteration can proceed.

Total Energy

Like V_{eff}, the computation of the total energy in a crystal requires careful consideration due to the long range nature of the Coulomb interaction and resulting divergent terms. In this case, the electron-electron and ion-ion terms are divergent and positive, while the electron-ion term is divergent and negative. As in the computation of V_{eff}, a common approach involves the addition and subtraction of analytic neutralizing densities (see, e.g., Pickett, 1989; Fattebert and Nardelli, 2003). Alternatively, it may be noted that the replacement of the local parts of the ionic potentials by corresponding localized charge densities, as discussed above, yields a net neutral charge density $\rho = \rho_i + \rho_e$, and all convergent terms in the total energy. For sufficiently localized $\rho_{i,a}$, a quadratically convergent expression for the total energy in terms of Kohn-Sham eigenvalues ε_i is then (Pask and Sterne, 2004)

$$\begin{aligned} E_{tot} = \sum_i f_i \varepsilon_i + \int_\Omega d\mathbf{x}\, \rho_e(\mathbf{x}) \left(V_L^{in}(\mathbf{x}) - \tfrac{1}{2} V_C(\mathbf{x}) - \varepsilon_{XC}[\rho_e(\mathbf{x})] \right) \\ - \tfrac{1}{2} \int_\Omega d\mathbf{x}\, \rho_i(\mathbf{x}) V_C(\mathbf{x}) + \tfrac{1}{2} \sum_a \int_{R^3} d\mathbf{x}\, \rho_{i,a}(\mathbf{x}) V_{i,a}^L(\mathbf{x}), \end{aligned} \quad (21)$$

where V_L^{in} is the local part of V_{eff} constructed from the input charge density ρ_e^{in}, V_C is the Coulomb potential associated with ρ_e, i.e., $\nabla^2 V_C = 4\pi(\rho_i + \rho_e)$, ε_{XC} is the exchange-correlation energy density, i runs over occupied states with occupations f_i, and a runs over atoms in the unit cell.

Figure 4 shows the convergence of FE results to well converged PW results as the number of elements in each direction of the wavefunction mesh is increased in a self-consistent GaAs calculation at an arbitrary k point, using the same pseudopotentials (Hartwigsen et al., 1998) and exchange-correlation functional. As in the PW method, higher resolution is employed in the calculation of the charge density and potential (twice that employed in the calculation of the of the wavefunctions, in the present case). The rapid, variational convergence of the FE approximations to the exact self-consistent solution is clearly manifested: the error is strictly positive and monotonically decreasing, with an asymptotic slope of ~ -6 on a log-log scale, indicating an error of $O(h^6)$, where h is the mesh spacing, consistent with the cubic completeness of the basis. This is in contrast to FD approaches where, lacking a variational foundation, the error can be of either sign and may oscillate.

Outlook

Because FE bases are simultaneously polynomial and strictly local in nature, FE methods retain significant advantages of FD methods without sacrificing the use of a basis, and in this sense, combine advantages of both PW and FD based approaches for *ab initio* electronic structure calculations. In particular, while variational and systematically improvable, the method produces sparse matrices and requires no computation- or communication-intensive transforms; and so is well suited to large, accurate calculations on massively parallel architectures. However, FE methods produce generalized rather than standard eigenproblems, require more memory than FD based approaches, and are more difficult to implement. Because of the relative merits of each approach, and because FE based approaches are yet at a relatively early stage of development, it is not clear which approach will prove superior in the large-scale *ab initio* electronic structure context in the years to come (Beck, 2000). Early non-self-consistent applications to *ab initio* positron distribution and lifetime calculations involving over 4000 atoms (Pask et al., 2001) are promising indications, however, and development and optimization of FE based approaches for a range of large-scale applications remains a very active area of research.

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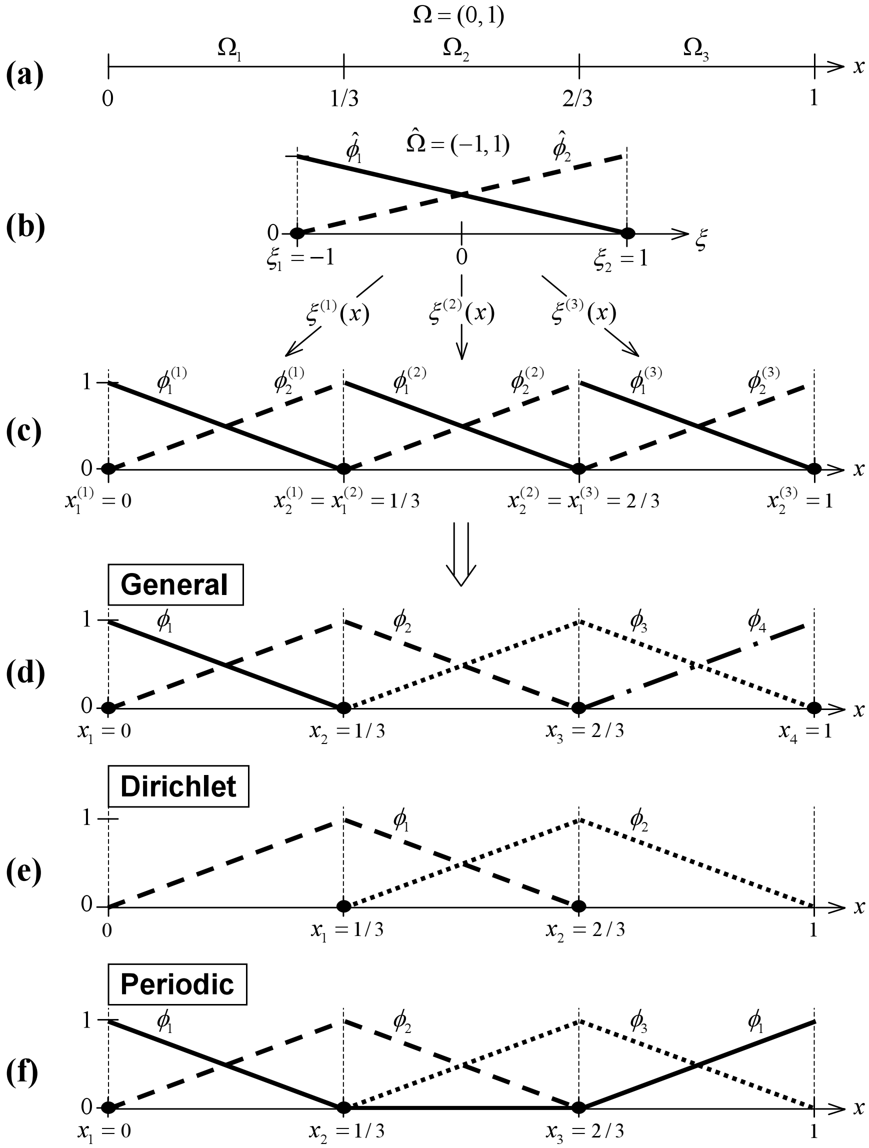
(a)
Ω = (0,1)
Ω₁
Ω₂
Ω₃
x
0
1/3
2/3
1
(b)
φ̂₁
Ω̂ = (−1,1)
φ̂₂
0
ξ₁ = −1
0
ξ₂ = 1
ξ
ξ⁽¹⁾(x)
ξ⁽²⁾(x)
ξ⁽³⁾(x)
(c)
1
0
φ₁⁽¹⁾
φ₂⁽¹⁾
φ₁⁽²⁾
φ₂⁽²⁾
φ₁⁽³⁾
φ₂⁽³⁾
x₁⁽¹⁾ = 0
x₂⁽¹⁾ = x₁⁽²⁾ = 1/3
x₂⁽²⁾ = x₁⁽³⁾ = 2/3
x₂⁽³⁾ = 1
x
General
(d)
1
0
φ₁
φ₂
φ₃
φ₄
x₁ = 0
x₂ = 1/3
x₃ = 2/3
x₄ = 1
x
Dirichlet
(e)
1
0
φ₁
φ₂
0
x₁ = 1/3
x₂ = 2/3
1
x
Periodic
(f)
1
0
φ₁
φ₂
φ₃
φ₁
x₁ = 0
x₂ = 1/3
x₃ = 2/3
1
x

Figure 1: 1D piecewise-linear FE bases. (a) Domain and elements. (b) Parent element and parent basis functions. (c) Local basis functions generated by transformations of parent basis functions to each element. (d) General piecewise-linear basis, generated by piecing together local basis functions across interelement boundaries. (e) Dirichlet basis, generated by omitting boundary functions. (e) Periodic basis, generated by piecing together boundary functions.

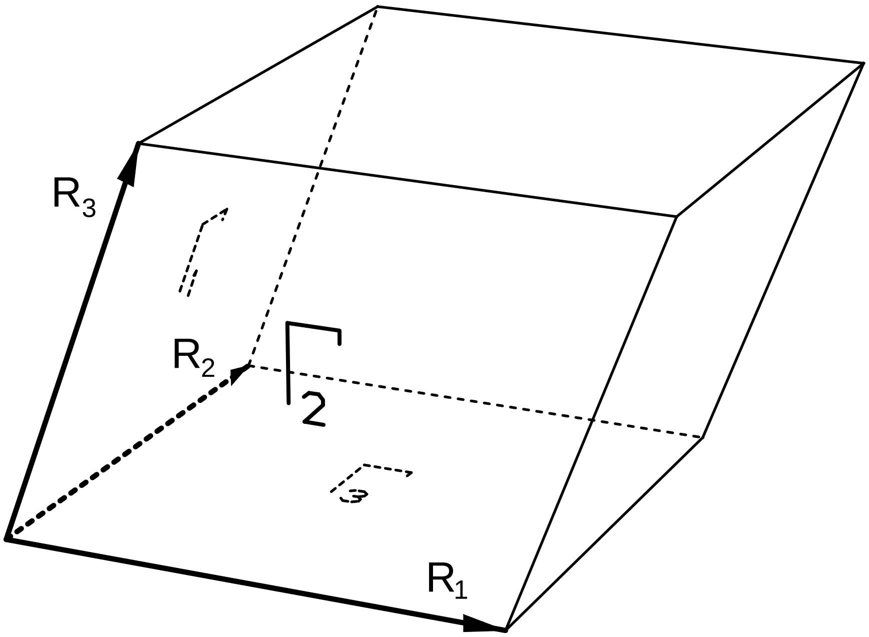

Figure 2: Parallelepiped unit cell (domain) Ω, boundary Γ, surfaces Γ_1–Γ_3, and associated lattice vectors $\mathbf{R}_1$–$\mathbf{R}_3$.

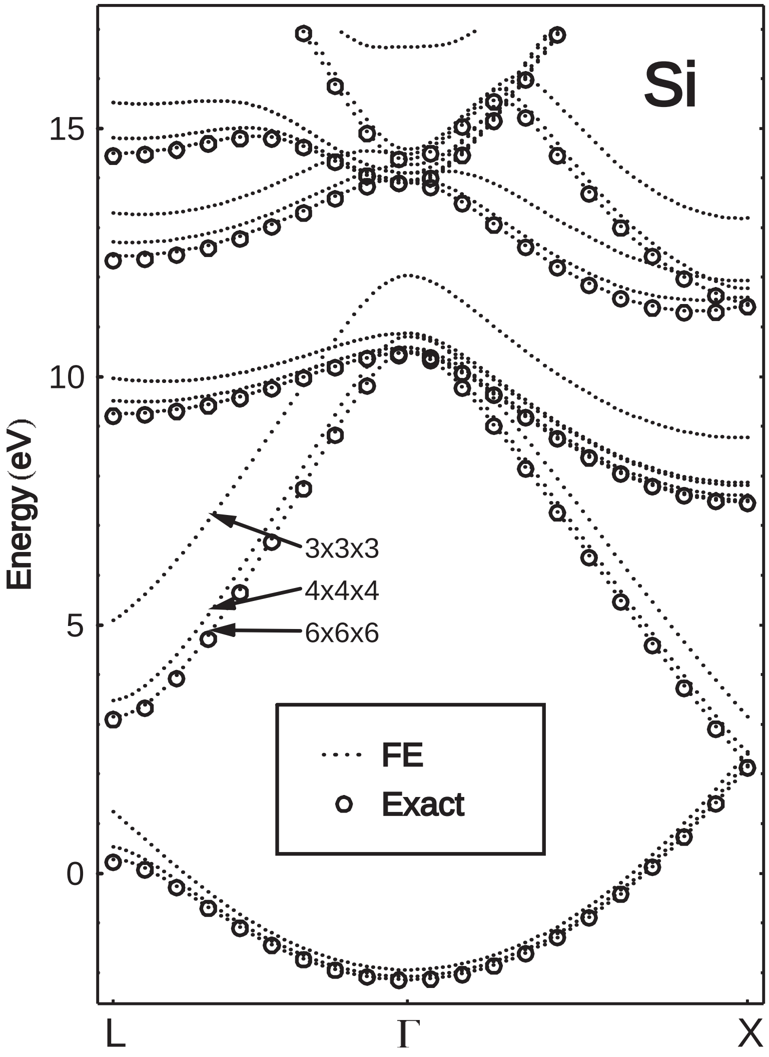

Figure 3: Exact and finite-element (FE) band structures for a series of meshes, for a Si primitive cell. The convergence is rapid and variational: the entire band structure converges from above, with an error of $O(h^6)$, where h is the mesh spacing.

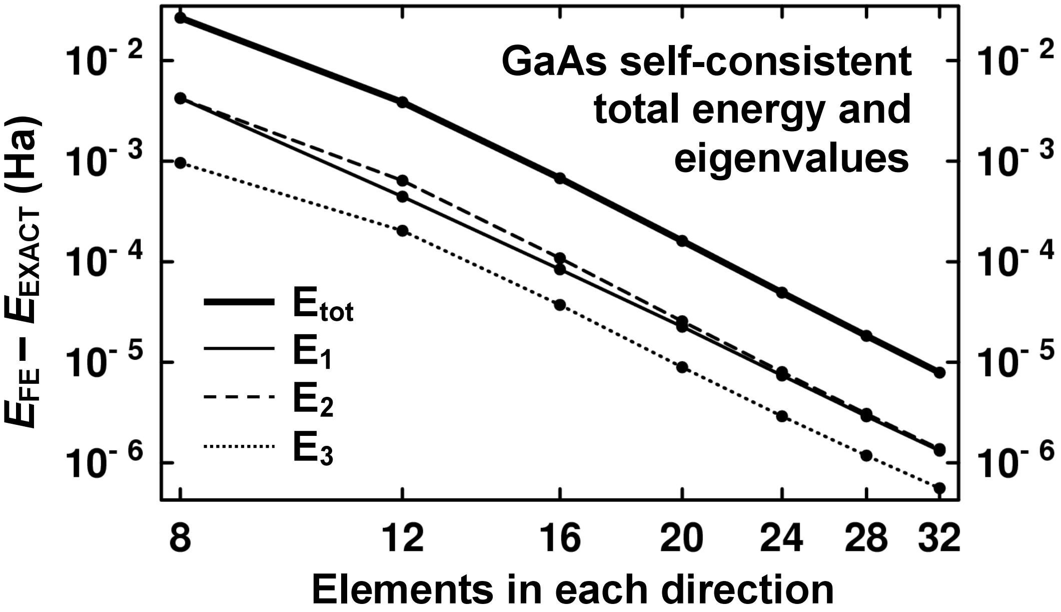

Figure 4: Convergence of self-consistent FE total energy and eigenvalues with respect to number of elements, for a GaAs primitive cell. As for a fixed potential, the convergence is rapid and variational: the error is strictly positive and monotonically decreasing, with an error of $O(h^6)$, where h is the mesh spacing.

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